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6. AUTHOR(S) Maurice Landstrass, Dale Moyer.				
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13. ABSTRACT (Maximum 200 words) Diodes were fabricated from in situ doped "N"-diamond/P-diamond layer structures. The "N"-dopants investigated were nitrogen and oxygen. The majority of the diodes fabricated to date have had either "leaky" characteristics or displayed high series resistance. As these diodes are designed to be gate electrodes, series resistance may be acceptable. SIMS measurements were performed on polycrystalline diamond films and diode structures to evaluate the doping efficiency of boron, nitrogen and oxygen. Boron doping efficiency was found to be very high with measured doping concentrations (polydiamond) of 5×10^{21} boron per cm^{-3} (based on a boron doped single crystal diamond calibration). The dopant concentrations, as measured by SIMS, of both nitrogen and oxygen was found to be too low, in the films analyzed, to create the desired N+(deep donor)/P+(boron) diamond diodes. The diode doping levels are limited by the currently achievable donor dopant concentrations to approximately $1.0 \times 10^{19} \text{ cm}^{-3}$. Electron channelling measurements were performed on boron doped diamond grown on type IIA natural diamond. These measurements confirmed the epitaxial relationship between CVD diamond layers grown in the plasma apparatus used for this study.				
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POLYCRYSTALLINE DIAMOND JUNCTION FIELD EFFECT TRANSISTORS (JFETS)¹

Progress Report
June 1, 1990
Maurice Landstrass, Dale Moyer

Results Summary

Diodes were fabricated from in situ doped "N"-diamond/P-diamond layer structures. The "N"-dopants investigated were nitrogen and oxygen. The majority of the diodes fabricated to date have had either "leaky" characteristics or displayed high series resistance. As these diodes are designed to be gate electrodes, series resistance may be acceptable. SIMS measurements were performed on polycrystalline diamond films and diode structures to evaluate the doping efficiency of boron, nitrogen and oxygen. Boron doping efficiency was found to be very high with measured doping concentrations (polydiamond) of 5×10^{21} boron per cm^3 (based on a boron doped single crystal diamond calibration). The dopant concentrations, as measured by SIMS, of both nitrogen and oxygen was found to be too low, in the films analyzed, to create the desired N+(deep donor)/P+(boron) diamond diodes. The diode doping levels are limited by the currently achievable donor dopant concentrations to approximately $1.0 \times 10^{19} \text{ cm}^{-3}$. Electron channelling measurements were performed on boron doped diamond grown on type IIA natural diamond. These measurements confirmed the epitaxial relationship between CVD diamond layers grown in the plasma apparatus used for this study.

Introduction

Because of its large band gap diamond has special attraction as a semiconductor material. Diamond based semiconductor devices should be able to operate at high temperatures and at high frequencies and should, in principle, be superior to devices fabricated in gallium arsenide. In addition the wide band gap should also make diamond significantly more immune to the effects of ionizing radiation as compared to other common semiconductors.

A major requirement is the need for dopant and device design technology specific to the unique requirements of diamond.

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TECHNICAL OBJECTIVES

The overall objective of this program is to develop a diamond JFET technology through optimization of junction properties. The primary approach is to control the built in junction voltage through nitrogen doping, and to control junction edge leakage with a passivation technology based on selective oxidation.

Technical Progress

Diamond Film Growth (General)

The desired device structure is composed of three layers; high resistivity diamond substrate, boron doped diamond active layer, and nitrogen doped diamond gate layer. Each of these layers impact the diode properties of the of the proposed JFET gate. Due to the very high doping efficiency of boron the three layers were grown in three separate reactors. This was necessary due to the high resistivity requirements of both the substrate and gate layer.

All boron doped layers were grown in a DC plasma reactor using mixtures of hydrogen, methane, and diborane gases. Nitrogen doped layers were also grown in a DC plasma reactor using mixtures of hydrogen, methane, and ammonia gases. Oxygen doped layers were grown in a microwave driven plasma reactor using mixtures of hydrogen, methane, and oxygen gases.

Electron channelling measurements were performed on diamond single crystals placed in the growth reactor during growth of the polycrystalline diamond films. Channelling measurements confirmed the epitaxial relationship of growth on these substrates.

Diamond Doping

Figure 1 is a band diagram of the proposed JFET gate structure structure. This device imposes several requirements on the different layers:

1. The channel doping has to be as high as possible,
2. The sheet doping of the gate has to be approximately the sheet doping of the channel,
3. The gate layer (nitrogen doped) has to be as thin as possible.

Boron Doping

The "heavy doping" requirement comes from the very high boron dopant activation energy. The activation energy boron in diamond is a function of dopant concentration and can approach reasonable values only at high doping levels. In a JFET the gain is proportional to conductivity per dopant atom and it is the total dopant concentration, independent of ionization, that is important. As a result of this effect in diamond, impurity ionization energy reduction is a first order design consideration of a doped channel JFET.

Figure 2 is a plot of the injected diborane to methane gas concentration ratio versus film resistivity. The resistivity plot in Fig. 2 exhibits a well behaved linear dependence on diborane concentration throughout the range plotted. This behavior suggests simple dopant incorporation on substitutional lattice sites without significant precipitation. The high concentration films were investigated by SIMS and found to contain $5.0 \times 10^{21} \text{cm}^{-3}$ boron. This concentration suggests massive precipitation of boron yet this conclusion is not supported by the other data. This value was calculated from data measured on a SIMS calibration standard which consisted of a boron doped natural single crystal diamond. Diamond has a very high atomic density of $1.75 \times 10^{23} \text{cm}^{-3}$ when compared to $5.0 \times 10^{22} \text{cm}^{-3}$ for silicon. SIMS is a precise technique with a long history in the analysis of silicon and gallium arsenide, but its use on diamond is new, especially so for CVD diamond films. Even when adjusted for the high atom density, the concentration of 2.8 atomic% boron in diamond is an exceptionally high value. While this value is comparable to the high temperature solid solubility of arsenic in silicon (4.0 atomic%) and that of boron in silicon (1.0 atomic%), low temperature CVD films typically do not achieve these high doping densities. The SIMS data appears to be in conflict with the well behaved dependence of film resistivity versus gas composition. Both the SIMS data and the resistivity are however in general agreement with published data^{1,2}. This will have to be resolved using different SIMS standards.

A calculation of the doping density calibrated from the measured endpoint gives a doping range of $5.0 \times 10^{21} \text{cm}^{-3}$ to $2.0 \times 10^{18} \text{cm}^{-3}$. From other work^{1,2} there is significant reduction in the boron activation energy in this dopant range. One of the key benefits of the JFET approach is that it provides a way to make a gate junction to a highly doped channel region. All devices have been fabricated from highly boron doped layers with an emphasis on dopant densities above $1.0 \times 10^{20} \text{cm}^{-3}$.

Nitrogen Doping

The second and third requirements for this device rely on controlled nitrogen doping of the gate layer. Nitrogen doping is not as straightforward to characterize as boron doping due to its electrical role as a deep donor. At normal temperatures deep donors are not ionized and do not create n-type conductive layers in proportion to the doping density. SIMS is the only technique that we have used that is readily able to determine the nitrogen doping density.

Figure 3 is a SIMS profile of a polydiamond pn junction doped with nitrogen and boron. The layers were grown to have the exact energy band structure as depicted in Fig. 1. The boron side was grown in a methane, hydrogen and diborane gas mixture with an 8000ppm boron to carbon concentration. The nitrogen doped side was grown in a methane, hydrogen and ammonia gas mixture with a 2.5% atomic nitrogen to carbon concentration. Both doped layers were grown on top of a 0.4 μm layer of undoped diamond. Figure 3 illustrates that the specific impurity incorporation varies strongly with dopant species when comparing boron to nitrogen.

From the data shown in Fig. 3, boron incorporates into the diamond lattice at a concentration proportionally higher than the gas phase concentration while nitrogen incorporates at substantially lower levels than the gas phase concentration. An interesting feature of these impurity profiles is the large concentration of nitrogen in the boron doped layer. The boron doped layer was grown in a gas ambient containing no intentionally added nitrogen. The boron doping reactor contained a 500 ppm nitrogen to carbon concentration in the gas phase as calculated from the specified feed gas impurity levels. The evidence suggest that the incorporation efficiency can be strongly dependent on the other dopants present in the diamond film.

The SIMS data in Fig. 3 clearly indicates that the structure fabricated does not meet the design requirements of a highly nitrogen doped diamond layer. The layer doping is far too low compared to the boron doped layer. As discussed above it is not desirable to decrease the boron doping so that device optimization demands a more efficient way to incorporate nitrogen. These results suggest that for CVD diamond films a co-dopant is necessary to achieve the high donor concentrations required for this device design.

Oxygen Doped Diamond

Oxygen is a double donor in silicon with unpredictable behavior. The electronic properties of oxygen dissolved in diamond are entirely unknown. Recently it has been reported that diamond films grown in an oxygen containing ambient behave functionally similar (as described above) to a diamond layer heavily doped with deep donors; i.e. permits a good junction to be made to material that otherwise would make leaky diodes³. Oxygen has an advantage over nitrogen as a dopant for CVD diamond in that films grow in oxygen ambients up to 50% by volume (flame growth). The compatibility allows for potentially higher dissolved oxygen concentration than with nitrogen. SIMS was performed on two samples grown in oxygen ambients, one in CO and one in O₂ with a 0.5 C/O ratio. The "dissolved" oxygen concentrations were $7.0 \times 10^{17} \text{cm}^{-3}$ and $2.0 \times 10^{18} \text{cm}^{-3}$. The word dissolved is in quotation marks due to the possibility that a large percentage of the oxygen is at the grain boundaries. The incorporation efficiency of oxygen using microwave growth is much lower than nitrogen using DC plasma growth.

Diamond Diode Measurements

Diodes were fabricated from wafers with the layer structure silicon/undoped diamond/boron doped diamond/nitrogen (oxygen) doped diamond. The diodes were fabricated by sputtering an array of aluminum dots on top of the nitrogen doped surface layer. Due to the surface layer special provision has to be made to contact the P+ boron doped diamond layer. "Ohmic" contact to the P+ diamond was made by subjecting some of the devices to a large current stress. This technique made the device conduct excess leakage current for both polarity directions but was substantially higher resistance than contacts made directly to the boron doped diamond layer. Figure 5 plots representative current-voltage (IV) characteristics from diodes fabricated using a 500Å oxygen doped surface layer and Fig. 6 plots similar results from diodes that use a 500Å nitrogen doped surface layer. Most devices displayed asymmetric IV characteristics though none of the devices had a high rectification ratio indicative of a 1 volt (or greater) built in junction voltage. The diodes in Figs. 5 and 6 were fabricated from boron doped diamond layers having a nominal doping of $\sim 1 \times 10^{20} \text{cm}^{-3}$ boron. Devices fabricated from structures employing thicker "n-type" regions had higher resistance and lower rectification ratios. Devices using thinner "n-type" regions were ohmic. From the above SIMS analysis the "n-layer" doping densities were too low to achieve a high built-in voltage using a thin "n-type" layer. Due to the high resistivity of "n-type"

regions doped with deep donors it is necessary for the layer to be thin enough so as not to dominate the IV characteristics. The low built in voltages are consistent with a Schottky barrier device formed with the aid of a thin low doped surface region. While this structure allows diodes to be made on heavily doped active regions it does not allow for the desired high built in voltages.

A nitrogen doping level of $4.5 \times 10^{19} \text{cm}^{-3}$ was used in the diode of Fig. 6 and an oxygen doping level of approximately $2.0 \times 10^{18} \text{cm}^{-3}$ was used in the diode of Fig.5. An anomalous feature of the data is that the oxygen doped diode behaves electrically as if the doping density is higher than the devices doped with nitrogen. SIMS data is strictly chemical in nature and consequently not directly in conflict with this result. This difference can be due to differing electrical states of nitrogen. Nitrogen has two common energy states: substitutional (i.e.type Ib) with a donor energy of approximately 2 volts or clustered (precipitated platelets) with a donor energy of about 4.5 volts(i.e. type Ia). In this device approach only the substitutional donors will be completely ionized. The multienergetic nature of nitrogen may be responsible for the the comparatively greater electrical activity of oxygen.

Conclusions

The major unresolved issue in diode construction is the incorporation of suitable high concentrations of n-type deep donor impurities. From the above data it is apparent here as in other works that boron dopes readily at any desired doping level. The device study has shown predictable trends in going from ohmic to rectifying behaviour with the insertion of an n-type junction layer and all indications are that if the doping density of the n-type layer could be increased the diode behaviour would improve. The major area of improvement and focus is consequently on raising the doping level of deep donors with an emphasis on nitrogen.

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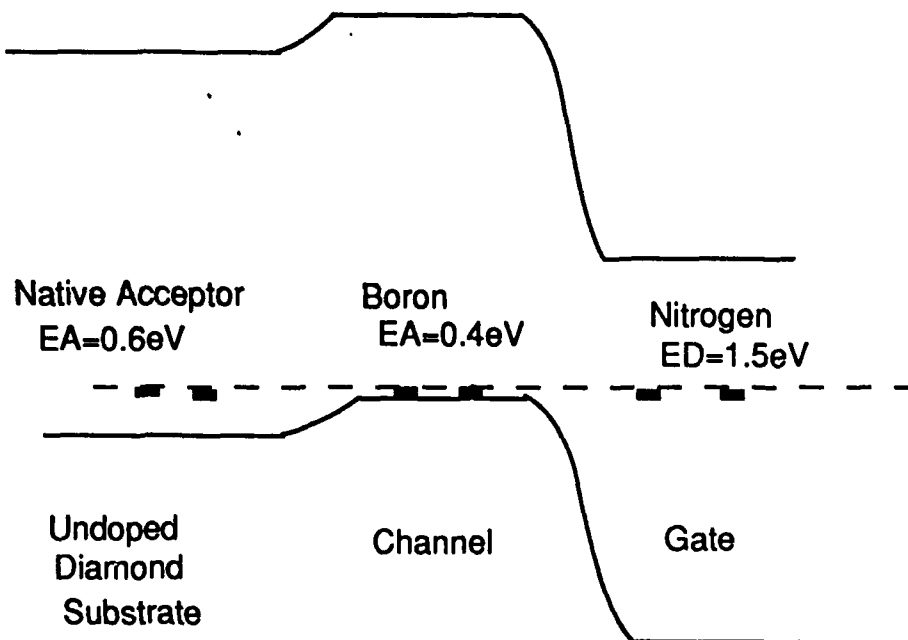


Figure 1. Hypothetical band diagram of a potential JFET configuration. In this figure the substrate Fermi level is controlled by a native acceptor defect level at 0.6 eV above the valence band, the channel is doped with boron, a "shallow" acceptor and the gate is doped with nitrogen, a deep donor with an energy level 1.5 eV below the conduction band. In an actual structure the native acceptors in the substrate would be compensated by nitrogen and have a resistivity and Fermi level as pictured in the above gate.

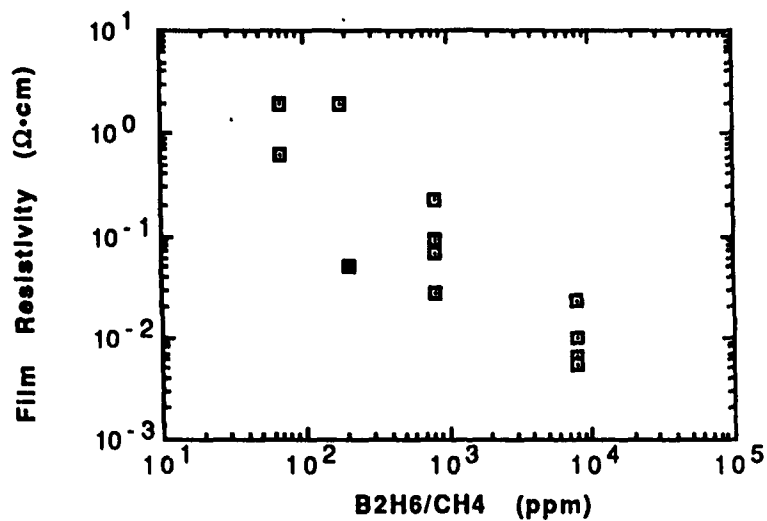


Figure 2. Diamond film resistivity versus the diborane to methane ratio present in the gas phase during layer growth.

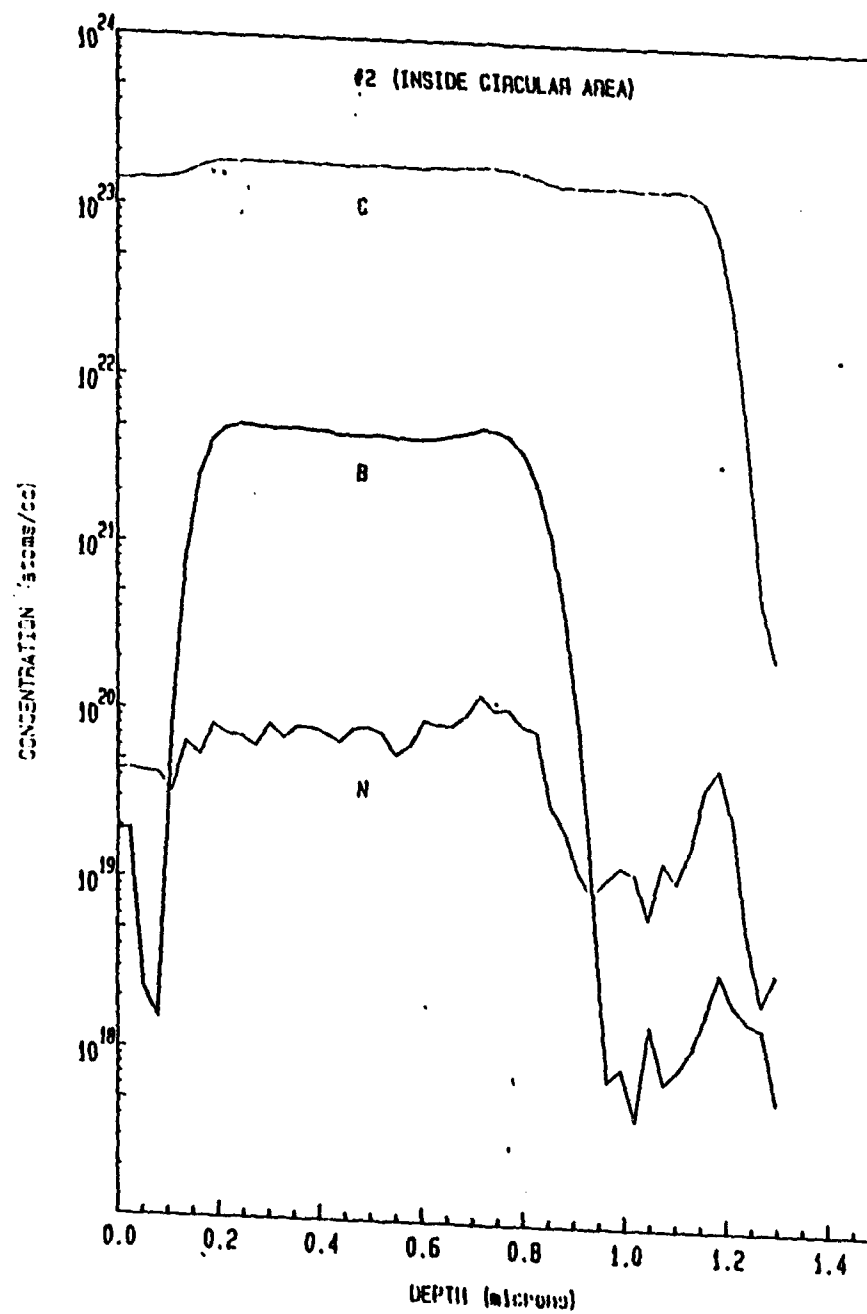


Figure 3 SIMS profile of the gate structure whose energy band structure is detailed in fig.1.

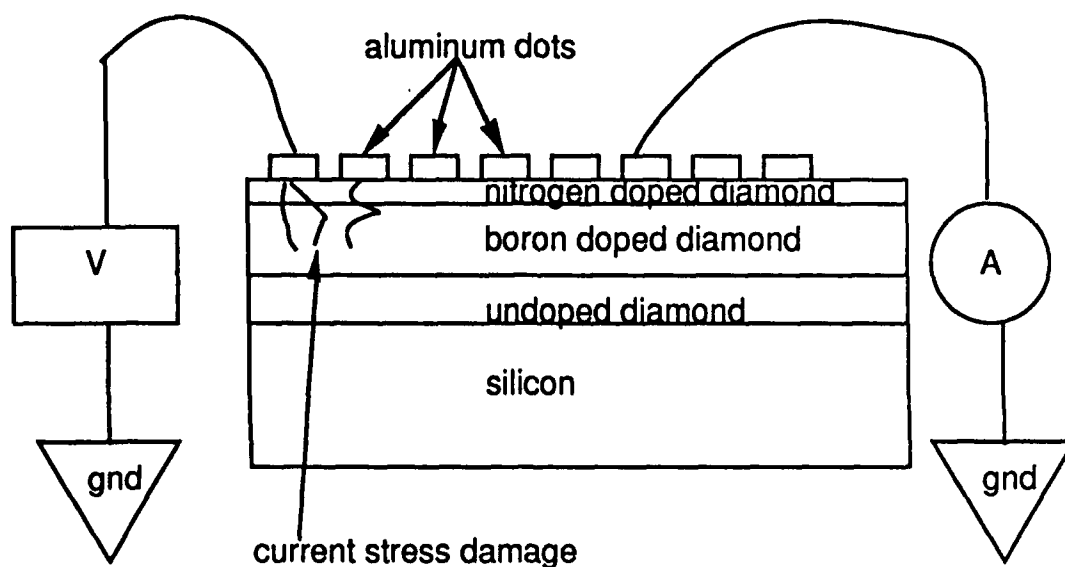


Figure 4. Diamond diode structure and schematic test set up.

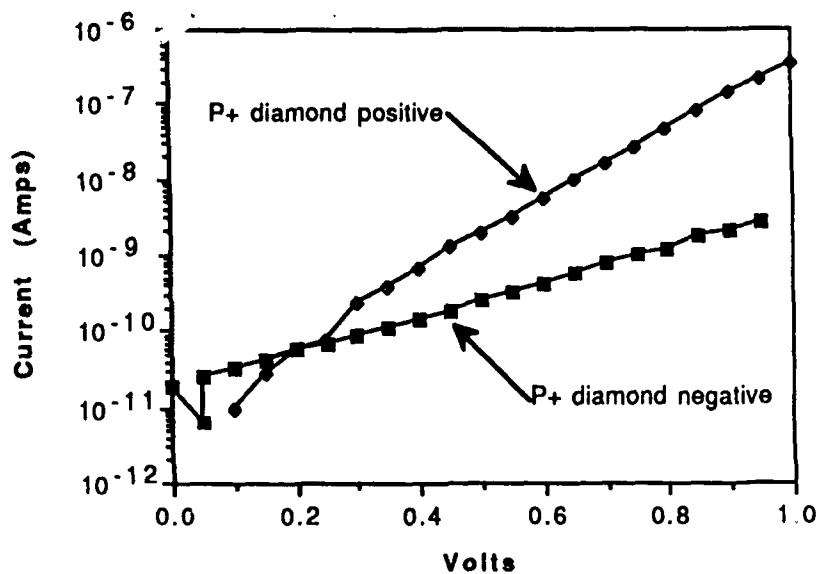


Figure 5. Current voltage characteristics measured on a diode using an oxygen doped n-type layer

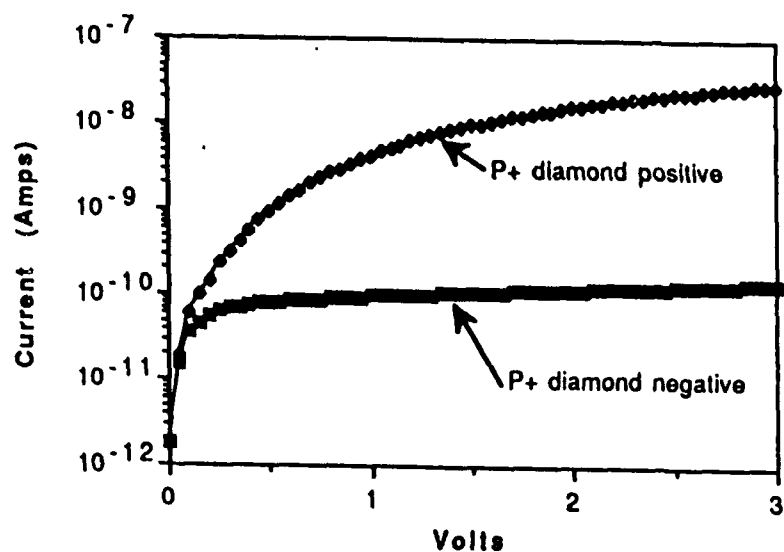


Figure 5. Current voltage characteristics measured on a diode using a nitrogen doped n-type layer.